H$_2$-assisted NH$_3$-SCR over Ag/Al$_2$O$_3$: An engine-bench study

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ABSTRACT

A combined catalyst system of Ag/Al$_2$O$_3$ and Fe-BEA was tested in a light-duty engine-bench for H$_2$-assisted NH$_3$-SCR. Ag/Al$_2$O$_3$ was used to provide a high low-temperature activity, while Fe-BEA can provide a high activity at higher temperatures without the need to co-feed H$_2$. The catalysts were combined in a sequential dual-brick layout and compared to Ag/Al$_2$O$_3$ and Fe-BEA only. The aim of the study was to investigate the performance of the catalysts in real life exhaust in contrast to synthetic gas. The catalysts were both tested during stationary and transient conditions. Transient testing was carried out with the New European Driving Cycle (NEDC). Laboratory tests were performed to complement the results from engine tests. Ag/Al$_2$O$_3$ showed a lower NO$_x$ conversion in stationary engine tests than expected. This was investigated further in a laboratory test set-up and was attributed to deactivation by soot and/or Ag oxidation, low H$_2$ levels and low specific catalyst loading. NO$_2$ increased the catalytic activity at below 250 and above 300 °C. For the combined systems, it was preferred to have Fe-BEA in an upstream position of Ag/Al$_2$O$_3$ compared to the opposite. The high engine out NO$_2$/NO$_x$ ratio, giving fast-SCR over the Fe-BEA, was believed to be the reason. At low temperature, the activity over the combined systems was higher than that for the individual catalysts showing that there were synergy effects of combining Ag/Al$_2$O$_3$ and Fe-BEA. This was also seen in the transient tests. However, the overall cycle NO$_x$ conversion was low due to very demanding conditions with a lot of the NO$_x$ being emitted at below 150 °C. The order of performance based on an overall conversion during the NEDC was dual-brick with Ag/Al$_2$O$_3$ upstream = Ag/Al$_2$O$_3$ only > dual-brick Fe-BEA upstream > Fe-BEA only. The Ag/Al$_2$O$_3$ containing layouts showed a noticeable NO$_x$ conversion from the start of the cycle, i.e. before any NH$_2$ or H$_2$ was dosed. We believe that the NO$_x$ conversion seen came from NO$_x$ storage on the Ag/Al$_2$O$_3$.

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1. Introduction

The upcoming Euro 6 and Euro VI emissions legislation for light- and heavy-duty diesel vehicles in Europe is very strict. It calls for large reductions of, among others, NO$_x$. It is well accepted that some type of exhaust after treatment will be needed for light-duty vehicles, as has been the case for heavy-duty vehicles for many years. For heavy-duty vehicles selective catalytic reduction (SCR) has almost completely penetrated the market. For light-duty vehicles there are other options in addition to SCR, with lean NO$_x$ traps (LNT) being the main one; SCR catalyst and LNT can also be combined [1]. Today there are light-duty passenger cars equipped with SCR being sold in Europe that meet Euro 6 standards. Another wide-spread technique is exhaust gas recirculation (EGR) which often is used together with SCR on heavy-duty vehicles or as a single measure to reach present NO$_x$ legislation (Euro 5) on light-duty

vehicles. EGR lowers the oxygen concentration and temperature in the engine cylinder which reduces NO$_x$ formation [2].

The main challenge for the NO$_x$ removal both for light- and heavy-duty vehicles is the low-temperature activity (<200–250 °C). Today's SCR catalysts, e.g. vanadia-based and Fe-zeolites, are efficient at higher temperatures [3]. Cu-zeolite type catalysts have been reported to have very promising low-temperature activity [4–6]; chabazite or chabazite-like structures are especially interesting due to their excellent hydrothermal stability [7–9]. Platinum group metal-based catalyst has also been proposed but suffers from too low selectivity to N$_2$ and a too narrow temperature window of operation [10,11]. Ag/Al$_2$O$_3$ is a promising candidate that has been reported to have high low-temperature activity, when H$_2$ is co-fed with either hydrocarbons (HC) [12–14] or NH$_3$ as the reductant [15,16]. We have previously investigated the mechanism [17,18] and sulfur tolerance [19,20] of NH$_3$-SCR with H$_2$ over Ag/Al$_2$O$_3$ and showed a promising low-temperature activity and stability of the catalyst. A large draw-back of NH$_3$-SCR over Ag/Al$_2$O$_3$ is that the catalyst is inactive without H$_2$ in contrast to HC-SCR which is active from 250 to 300 °C even without H$_2$ [12–14]. Thus, we combined

Ag/Al_2O_3 with Fe-BEA in a previous study and showed that the amount of H_2 needed can be reduced without sacrificing the activity over the combined catalyst system [21]. Fe-BEA shows high activity from 250 to 300 °C [5,6,22]. Since diesel exhaust contains a lot more compounds than are possible to include in simulated exhaust, the catalyst system has to be tested under real conditions to fully evaluate the potential of it. Compounds, such as unburned hydrocarbons, particulates, residues from engine lubricant oil and even traces of metal from engine wear [23] could potentially affect the catalyst performance. There is a number of reports that test Ag/Al_2O_3 in real diesel exhaust for HC-SCR [24–29]; to our knowledge, there are none using urea/NH_3 as the reductant. The reported NO_x conversions were dependent on the type of HC species used, HC/NO_x ratio, GHSV and amount of H_2 used.

In this study, we aim to investigate the performance of Ag/Al_2O_3, Fe-BEA and a combination of the two in the exhaust of a light-duty engine mounted on an engine dynamometer for H_2-assisted NH_3-SCR. We tested the catalysts both under stationary and transient conditions. Transient testing was made with the New European Driving Cycle (NEDC). Laboratory tests were performed to complement results from the engine tests.

2. Materials and methods

2.1. Catalyst preparation

Ag/Al_2O_3 catalyst (4 wt% Ag) was prepared by incipient wetness impregnation of $Si-Al_2O_3$ (Siralox 5/320, courtesy of Sasol Germany) with $AgNO_3$ (99.8% purity). The prepared catalyst was dried at room temperature and at 100 °C and later calcined at 500 °C. The Fe-BEA was a commercial 1 wt% Fe catalyst. The catalysts were washcoated onto cordierite monolith bricks (400 cpsi) to give the desired catalyst loading (120–160 g/l). We used 5.6 in. × 5.0 in. ($d \times h$) (2 l) bricks for engine testing and 4.9 cm × 7.6 cm ($d \times h$) (0.14 ml) bricks for laboratory tests. The catalyst bricks were dried at room temperature in flowing air and calcined at 500 °C for 2 h after the washcoating. Core samples, 4.9 cm × 7.4 cm ($d \times h$), were taken from the Ag/Al_2O_3 catalyst used in the engine tests and were tested in the laboratory test set-up.

2.2. Engine dynamometer testing

A 2.0 l, 120 kW, five-cylinder direct-injected Volvo diesel engine equipped with EGR was used for engine dynamometer testing. The engine was rated to Euro 5 emission standard. A standard low-sulfur (<10 ppm) diesel was used. The engine was mounted on a Horiba DYNAS$_3$ HT250 engine dynamometer test rig. The two catalyst bricks (4 l in total volume) were placed directly after each other, approximately 75 cm after the engine. NH_3 and H_2 were dosed approximately 30 cm before the catalysts. The temperature was measured before and after the catalysts. The exhaust gas was analyzed by two Horiba MEXA 7170D and one FTIR (Gasmet 4000). Together, they can measure NO, NO_2, N_2O, NH_3, CO, CO_2, H_2O, O_2 and hydrocarbons (HC). HC was measured as total HC based on C_1-equivalents.

One MEXA was placed directly after the engine and used as a reference of engine out concentrations. The second MEXA and the FTIR were coupled to the same sample line; sampling could either be carried out before or after the catalysts by switching the sample point in the engine dynamometer control program. Fig. 1 shows a schematic picture of the set-up. NO_x (NO and NO_2), N_2O, NH_3 and H_2O were measured by FTIR and HC, O_2, CO and CO_2 by MEXA (unless stated otherwise). Conversions ((NO_x, NH_3 and HC) were calculated by comparing catalyst inlet and outlet levels by switching the sample point.
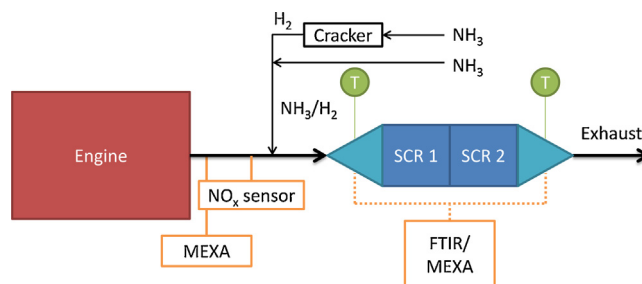

Fig. 1. Schematic layout of engine-bench test set-up.

NH_3 was supplied from a gas bottle by a mass flow controller. H_2 was supplied by feeding NH_3 to a cracker, where it was converted to H_2 and N_2; some unreacted NH_3 also remained in the stream. The NH_3 flow to the cracker was controlled by a mass flow controller. During stationary tests, the amount of NH_3 and H_2 dosed was controlled by online calculations from the actual NO_x concentrations (measured by NO_x sensors) and flow with fixed NH_3 (ammonia to NO_x ratio, ANR) and H_2 (hydrogen to NO_x ratio, HNR) to NO_x ratios. During transient testing, NH_3 and H_2 dosing were either controlled by online calculations, as in the case of stationary testing with dosing starting when the exhaust gas temperature was above 150 °C, or as pre-calculated values based on NO_x and flow inlet values from previous reference tests. The pre-calculated values were used to allow dosing from 120 °C by circumventing the low-temperature limit of reductant dosing below 150 °C due to an electronic shut down of the NO_x sensors used for calculating the amount NH_3 and H_2 to be dosed. The same ANR and HNR, 0.8 and 2, respectively, were used in all tests.

Table 1 shows the engine settings and relevant data for the six stationary points tested. The points were chosen to give comparable NO_x concentrations and total flows. The inlet NO_x levels varied significantly, they were in general lowest in the first test (Ag-only). At each point, temperature, NO_x level and NH_3 level were allowed to reach steady-state before changing the conditions. Tests were performed with (NH_3 and H_2 dosing) and without co-feeding of H_2 (only NH_3 dosing). Measurements were made before and after the catalysts. For transient tests, the New European Driving Cycle (NEDC) was used. It comprises four urban cycles and one extra urban cycle (highway cycle) and has a total road distance of 11 km and takes 1180 s to complete. Fig. 2 shows the road speed during the NEDC and the engine out temperature. The engine was operated under high speed and low throttle conditions (3500 rpm/0%) for approximately 20 min prior to the start of the NEDC to cool
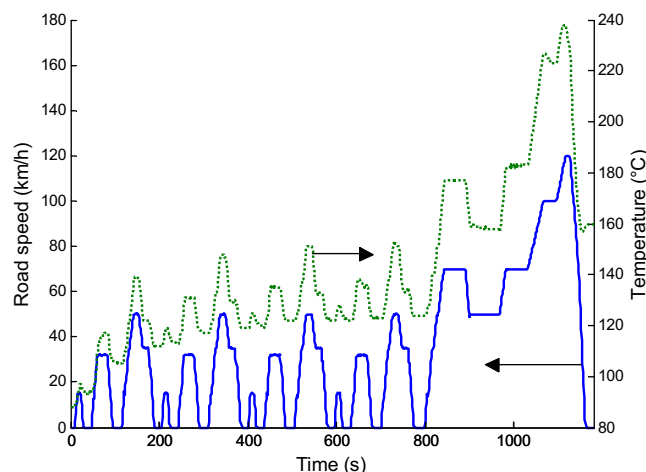

Fig. 2. NEDC, road speed and actual temperature.

Table 1
Data for steady-state stationary engine points, GHSV based on a total of 4 l catalyst.

T (°C)	Engine settings		GHSV (h^{-1})	NO_x (ppm)	O_2 (%)	H_2O (%)	CO_2 (%)	CO (ppm)	HC[a] (ppm)
	Speed (rpm)	Torque (N m)							
160	2800	15	33,000	140–150	16	4.0	3.4	1000	240–280
180	2800	30	34,000	160–180	15	4.6	4.5	840	170–220
220	2800	50	36,000	190–230	14	5.5	5.3	560	100–150
270	2740	75	34,000	150–210	11	7.0	6.9	280	60–100
340	2330	125	33,000	130–160	7.8	9.2	9.6	200	30–60
400	1835	200	33,000	160–210	5.2	11	11	480	16–25

[a] The level was in the higher range for Ag-only.

down the exhaust system. The inlet gas temperature at the start of the cycle was 60 °C.

Four layouts were tested: Ag/Al_2O_3 (Ag-only), Fe-BEA (Fe-only), Fe-BEA upstream of Ag/Al_2O_3 (dual-brick-Fe/Ag) and Ag/Al_2O_3 upstream of Fe-BEA (dual-brick-Ag/Fe). A total of two bricks (4 l of catalysts) was used in all cases; either two of the same type (Ag- and Fe-only) or one of each type (dual-brick-Fe/Ag and dual-brick-Ag/Fe).
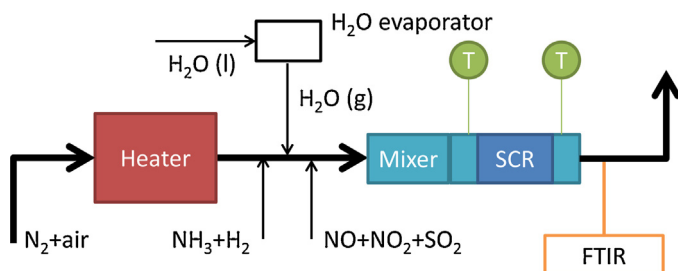
2.3. Laboratory testing

Testing was also carried out in a laboratory set-up. Fig. 3 shows a schematic picture of the set-up. N_2 and air were first heated in a gas heater before the desired feed gases were added. The resulting feed was passed through a mixer to ensure a homogenous composition before entering the reactor and the monolithic catalyst. All gases and liquid H_2O were controlled with mass flow controllers. All lines after the heater were made of steel. H_2O was evaporated by passing liquid H_2O to a heated metal block, where it was rapidly evaporated; the lines after the evaporator was heated to 180 °C to avoid condensation. The temperature was measured by thermocouples before and after the catalyst.

A standard feed of 500 ppm NO, 500 ppm NH_3, 1000 ppm H_2, 8% O_2, 12% H_2O and balance N_2 was used for activity testing. NO was mixed with air to allow oxidation to NO_2 in order to investigate the influence of NO_2 on the reaction. NO_2/NO_x ratios of 0.25, 0.5, 0.75 and 0.95 were tested and compared to the standard feed ($NO_2/NO_x = 0$). Tests were also performed without adding H_2. The outlet gas was analyzed by a FTIR (Gasmet 4000) after the catalyst. Inlet concentrations were taken from the given set-points (verified by empty reactor tests). The FTIR-lines were heated to 180 °C to avoid H_2O condensation and NH_4NO_3 formation. The GHSV was 30,000 or 33,000 h^{-1} depending on the size of the tested catalyst brick.

2.4. TPD

NH_3 and NO-TPD were carried out in a fixed-bed flow reactor, where 0.5 g of the powder catalyst (of a particle size of 150–300 μm) was used. The catalyst was treated in N_2 at 500 °C for 30 min. prior to adsorption of NO or NH_3. NO was adsorbed at 40 °C (2000 ppm, 10% O_2, balance N_2) and NH_3 at 150 °C (2100 ppm, balance N_2). Excess NO or NH_3 was removed by switching back to pure N_2, before the temperature was ramped up (2 °C/min) to 500 °C (NO-TPD) or 650 °C (NH_3-TPD) in a pure N_2 atmosphere.

3. Results and discussion

3.1. Stationary tests

Fig. 4 shows NO_x conversions for the four layouts tested (Ag-only, Fe-only, dual-brick-Fe/Ag and dual-brick-Ag/Fe) as a function of temperature for the NH_3 and H_2 dosing case during stationary tests. Ag-only showed an unexpectedly low NO_x conversion in the whole temperature range (compared to e.g. [21]). Fe-only showed a higher than expected NO_x conversion at 150 °C and a 90% NO_x conversion at 340 and 400 °C. The combined catalyst systems (dual-brick-Fe/Ag and dual-brick-Ag/Fe) showed an activity profile that was a combination of that of Ag/Al_2O_3 and Fe-BEA with a local maximum at 180 °C corresponding to that of Ag/Al_2O_3 and a sharp increase in activity at above 270 °C related to Fe-BEA. It was, as seen, preferred to have Fe-BEA as the upstream catalyst (dual-brick-Fe/Ag) compared to having Ag/Al_2O_3 upstream. This contradicts our previous results, where there was a clear advantage of having Ag/Al_2O_3 upstream [21]. We attributed this, among other things, to a complete NH_3 conversion over Fe-BEA giving a deficit of NH_3 over the downstream catalyst. In this study, no such unselective NH_3 oxidation was seen (Fig. 5). Fig. 5 shows that there were very small differences in NO_x conversion between NH_3 and H_2 dosing and only NH_3 dosing for Ag-only and the combined

Fig. 3. Schematic layout of laboratory set-up.
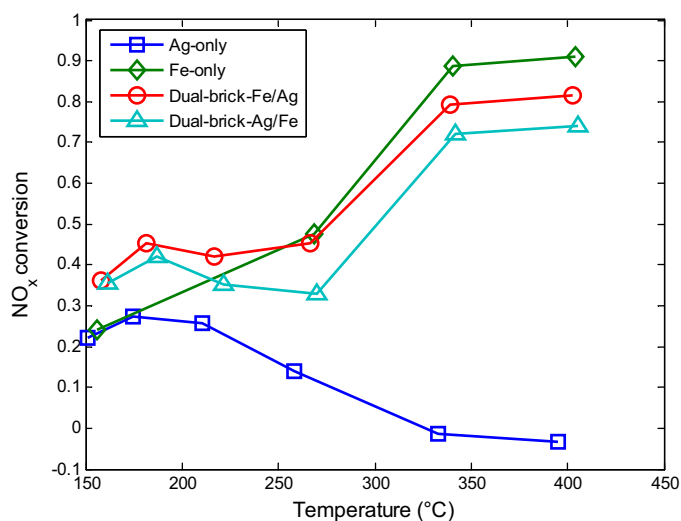
Fig. 4. Engine-bench stationary steady-state NO_x conversions as function of temperature for the different catalyst layouts. The layouts including Ag/Al_2O_3 are tested with NH_3 and H_2 dosing and Fe-only with only NH_3 dosing.
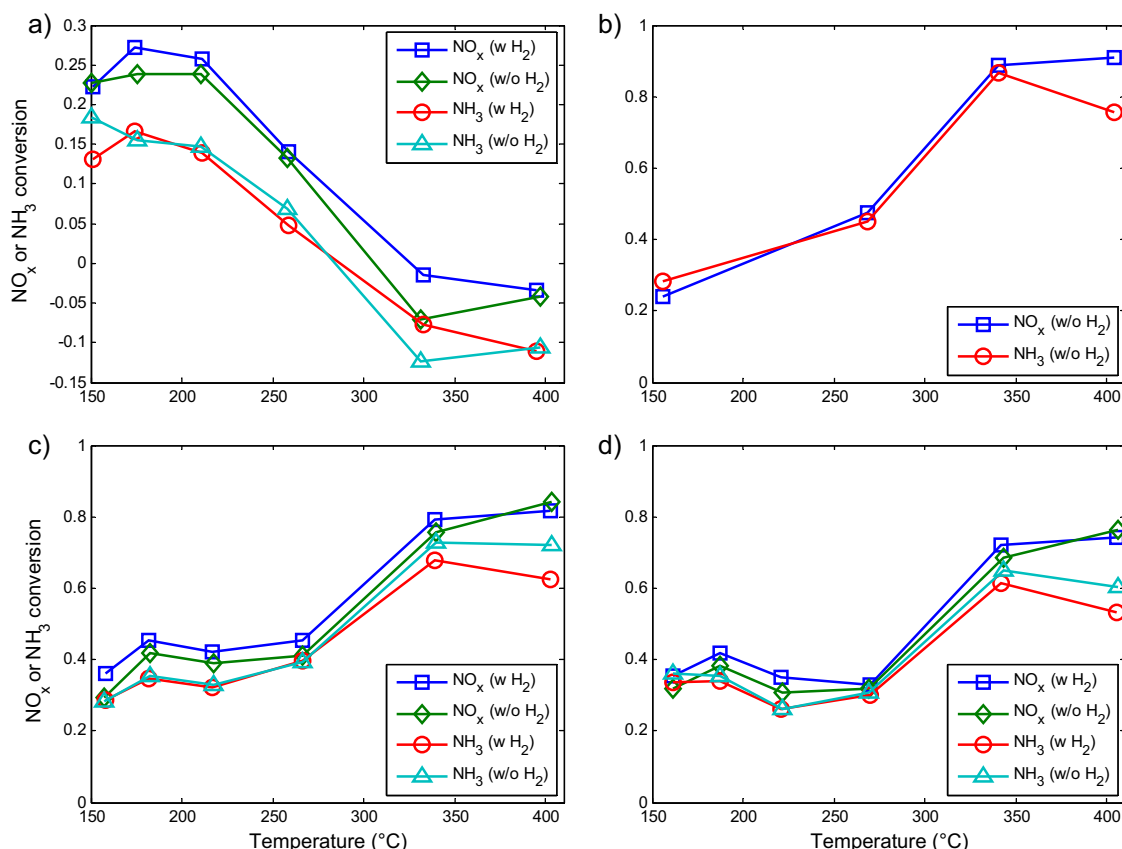
Fig. 5. Engine-bench stationary steady-state NO_x and NH_3 conversions as a function of temperature for (a) Ag-only, (b) Fe-only, (c) dual-Fe/Ag and (d) dual-Ag/Fe. The systems were tested both with NH_3 and H_2 dosing (w H_2) and with only NH_3 dosing (w/o H_2).

systems. Since the effect of H_2 is very pronounced [15], this was highly unexpected and will be discussed later.

The ratio between the amounts of converted NH_3 and converted NO_x over the catalysts varied between 0.8 and 1.2 and in most cases it was close to 1 for the Fe-BEA containing layouts, in good agreement with the expected results [5,6,22]. Most of the $deNO_x$ activity is believed to occur on the Fe-BEA (Fig. 4) for the combined systems. Thus, the somewhat low NH_3 conversion seen for the combined system (Fig. 5) can be explained by an overstoichiometric dosing of NH_3 due to unreacted NH_3 present in the H_2 stream from the

NH_3 to H_2 cracker (Fig. 1). Ag-only, on the other hand, showed lower values at up to $270\,^\circ$C (0.4–0.6); at higher temperatures, the NH_3 conversion was negative and the NO_x conversion was slightly negative giving large positive values. The low NH_3/NO_x ratio for Ag-only indicates that it is not only the main SCR reactions that were responsible for the NO_x conversion.

Fig. 6 shows the NO, NO_2, NO_x and NH_3 concentrations for Ag-only. NO_2 concentrations in and out were a bit higher, and NH_3 in was a bit lower relative to total NO_x compared to the other layouts. The inlet NO_2 level was very high, it is typically expected that some
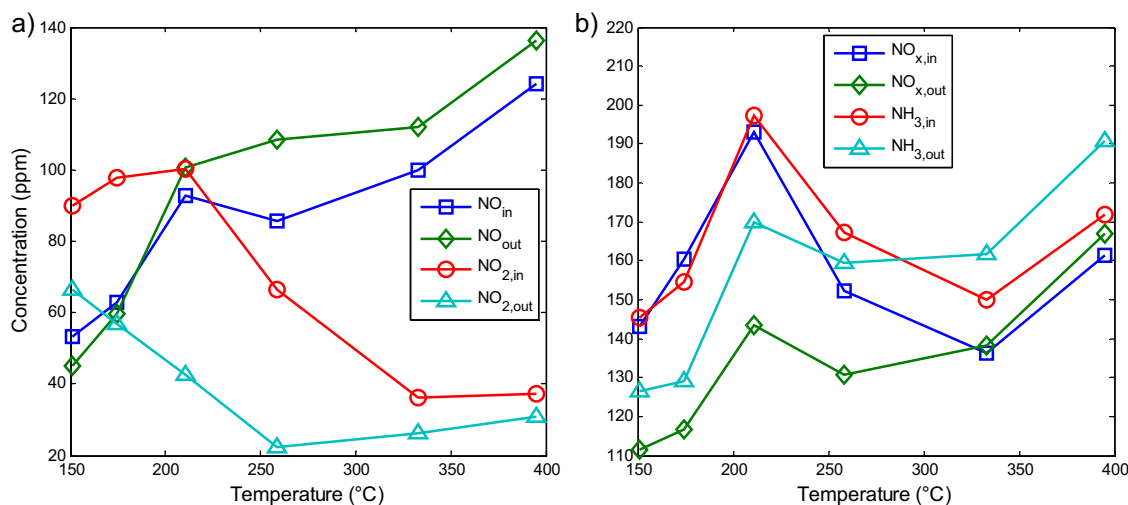

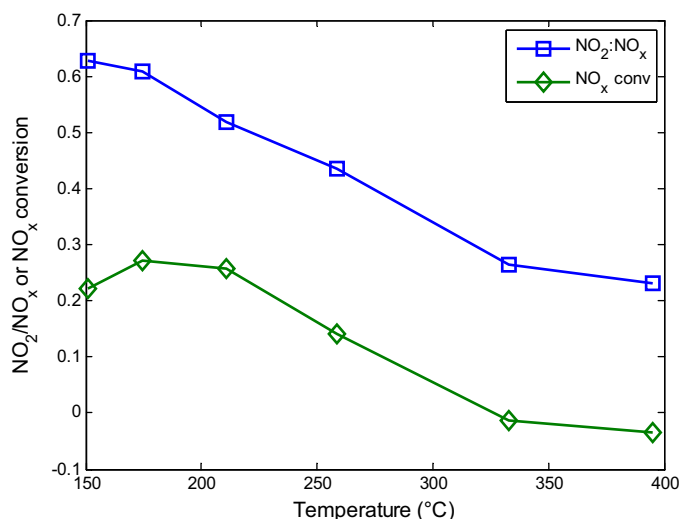**Fig. 6.** Engine-bench stationary steady-state concentrations as function of temperature for Ag-only with NH_3 and H_2 dosing.

Fig. 7. Engine-bench stationary steady-state NO_2/NO_x ratios vs. NO_x conversions as function of temperature for Ag-only, NH_3 and H_2 dosing.

10% of the total NO_x is NO_2. Here, the levels were up to 60% at the lowest temperatures and 18–20% at 400 °C. The high NO_2 levels are attributed to the high EGR rate, 60, 50, 40, 30, 20 and 20% seen for the six temperature points, respectively (low to high temperature). The air fuel ratios (AFR) roughly had the same values as the EGR rate. EGR lowers the peak temperature in the engine cylinders and thus the NO_x level [2]. However, NO_2 has been reported not to be affected to a larger extent which will increase the NO_2/NO_x ratio [30–32]. NO_x was primarily removed as NO_2 at the lowest temperatures (<250 °C) (Fig. 6). NO was produced over Ag-only from 220 °C and up by NO_2 to NO reduction. A close resemblance between NO_x conversion and NO_2 level for Ag-only (Figs. 4 and 6) can be seen. Fig. 7 shows the NO_2/NO_x ratio and NO_x conversion for Ag-only; there was a clear likeness of the two at temperatures above 200 °C, indicating a relation between the two. This was not seen for any of the other layouts (not shown).

Fe-BEA has, as other Fe-zeolites, been reported to be very active when equimolar amounts of NO_2 and NO are co-fed, so called "fast-SCR" [6,22]. The high NO_2/NO_x ratio allowing fast-SCR, which makes Fe-BEA more active than Ag/Al_2O_3, is believed to be the reason for the high deNO$_x$ activity seen for Fe-only and why Fe-BEA was preferred as the upstream catalyst (dual-brick-Fe/Ag) in the combined systems. Having Ag/Al_2O_3 upstream will mean that less NO_2 is present for fast-SCR over the Fe-BEA with a lower system deNO$_x$ activity as the consequence. Fast-SCR has also been reported to suppress NH_3 oxidation [22]. Our previous study [21] did, in contrast to this study, only have NO present as the NO_x compound. NO to NO_2 oxidation over Ag/Al_2O_3 which could later react over the Fe-BEA was, together with unselective NH_3 oxidation over Fe-BEA, believed to be the reasons why Ag/Al_2O_3 was preferred as the upstream catalyst in the previous study. The difference in feed gas composition is believed to explain the difference seen between the two studies.

The NH_3 outlet concentration was higher than the inlet concentration at above 300 °C, indicating NH_3 formation. Since all points are taken at steady-state and that the same analysis equipment was used for both inlet and outlet measurements, experimental errors can be excluded. Still, a simple N-balance between inlet and outlet NO_x and NH_3 shows an excess of N-containing species at the outlet, this can be considered close to the experimental uncertainty. NH_3 formation over Ag/Al_2O_3 has been reported in the literature [33–37]. The NH_3 formation was in these studies attributed to the reaction of NO with H_2 [33,34], hydrolysis of N-containing

hydrocarbons (without H_2) [35] or reaction of HC and NO_x [36]. In a preliminary test prior to the one reported here, NH_3 formation was observed during transient testing. No conclusive NH_3 formation could be seen in the present test. The difference between the preliminary test and the present test was the HC level. DiMaggio et al. [36] showed that NH_3 formation is dependent on H_2 level, temperature and C:N ratio. The higher HC level in the preliminary test (up to 2–2.5 times higher) could therefore be the reason why NH_3 formation was seen in that test and not in the present one. NH_3 formed over an upstream catalyst and then stored on the downstream catalyst, e.g. Fe-BEA, is similar to what has been proposed for combined LNT and SCR systems [38]. It can be a very interesting way to boost low-temperature activity and the potential problem of urea decomposition and formation of deposits at temperatures <190 °C [3]. Thus, further investigation of the potential NH_3 formation over Ag/Al_2O_3 is interesting but beyond the scope of this study.

This study also wanted to investigate if the hydrocarbons present in the exhaust could contribute to the total NO_x conversion by HC-SCR. Sitshebo et al. [28] reported that unburned HC present in the exhaust could give a noticeable NO_x conversion; especially when H_2 was present. It should be noted that the 4 wt% Ag catalyst used here might not be suited for HC-SCR. An optimal Ag loading for HC-SCR is often reported to be around 2 wt% [14,25,26]. No larger HC conversion over Ag/Al_2O_3 (Ag-only) was seen. Fe-BEA (Fe-only), on the other hand, showed a higher HC conversion, and it is reasonable to believe that the HC conversion seen for the combined systems comes from the Fe-BEA. Given the low NO_x conversion over Ag-only and the low ratio of reacted NH_3 to NO_x, HC-SCR might still contribute. This was also indicated by the low amount of reacted NH_3 to NO_x over Ag-only. The low NO_x and HC conversion, however, makes it hard to clearly see this.

The actual amount of NH_3 dosed during the tests was higher than the set-point (Fig. 6), especially when both NH_3 and H_2 were dosed due to the unreacted NH_3 in the stream from the cracker. It was even a bit higher for the combined systems (not shown). An overdosing of NH_3 is believed not to affect Ag/Al_2O_3 [18]. However, it might affect Fe-BEA and thus the combined systems [4–6,39]. Since no measurement of H_2 was possible, the actual amount dosed can only be estimated indirectly. The H_2 level was estimated both based on the given set-point to the H_2 dosing system and the amount of unreacted NH_3 in the stream from the cracker. Both estimations gave similar results. The estimated H_2 level dosed was a bit low due to the maximum NH_3 cracking capacity limit of the cracker system. In the worst cases (at 220 °C), the H_2/NO_x ratio was 1 (set-point HNR 2), in most other cases 1.4–1.6. The lack of H_2 will affect the activity, since Ag/Al_2O_3 is sensitive to H_2 concentration; especially in the region 200–300 °C [18] and can partly explain the low activity over Ag/Al_2O_3.

As stated above, the performance of Ag/Al_2O_3 was lower than expected, both in Ag-only and in the combined layouts. It was also unexpected that the NO_x conversion was very similar whether or not H_2 was co-fed. There was also an apparent relation between NO_2/NO_x ratio and NO_x conversion. Three possible explanations can be proposed: (1) a H_2 deficit of over the Ag/Al_2O_3, only allowing NO_x reduction via NO_2 [17]; (2) the catalyst was deactivated, not allowing the expected H_2-assisted NH_3 SCR to commence; and (3) the presence of NO_2 inhibits the performance of the catalyst. The latter could indirectly be due to NO_2 poisoning of NO active sites [14].

The H_2 concentration was low, as stated above, which will affect the activity of Ag/Al_2O_3 in a highly negative way. However, it should be high enough to show a higher difference in activity between NH_3 and H_2 dosing and only NH_3 dosing. Whether H_2 was available over the whole catalysts or not cannot, however, be concluded from these tests. Excessive H_2 oxidation in the first part
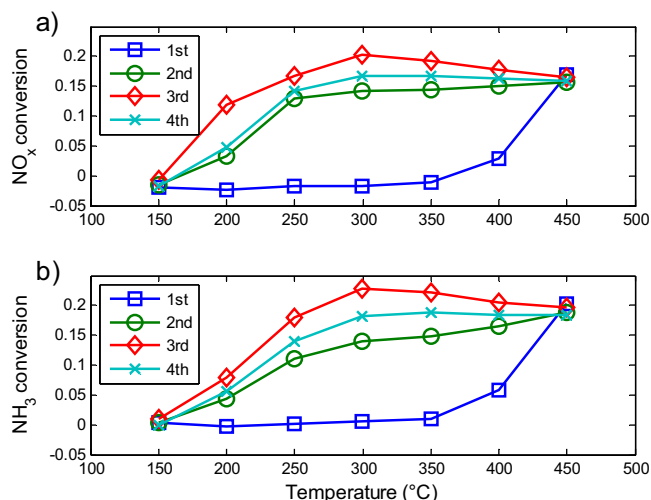
Fig. 8. Temperature dependency of NOx (a) and NH3 (b) conversion for core sample after engine tests. 1st test and 2nd test before and 3rd test and 4th test after regeneration (in situ at 500 °C and in oven at 550 °C). Reaction conditions: 500 ppm NO, 500 ppm NH$_3$, 1000 ppm H$_2$, 8% O$_2$, 12% H$_2$O and balance N$_2$, GHSV ~ 33,000 h^{-1}.

of the catalyst brick would give a H$_2$ deficit downstream. Several authors have shown that the presence of NO$_2$ can reduce the NO$_x$ conversion for HC-SCR, with or without H$_2$ present [13,14,40]. Other reports, on the other hand, have shown the opposite, they also showed that bare Al$_2$O$_3$ was active when NO$_2$ was fed [41,42]. A difference between the cited reports is the HC species used. The reports showing a positive effect [41,42] both used propene, while those showing no or negative effect ([13,14,40]) used saturated alkanes (propane or decane), which might affect the results. The HC present in the exhaust is a close match to the composition of the diesel fuel with mainly longer straight HC species. We have recently shown that Ag/Al$_2$O$_3$ (and Al$_2$O$_3$) was active for NH$_3$-SCR (without H$_2$), when mixtures of NO and NO$_2$ are used [17]. The activity was, however, much lower than for H$_2$-assisted NH$_3$-SCR of NO and limited to a maximum of 30% NO$_x$ conversion regardless of NO$_2$/NO$_x$ ratio. The stability of the catalyst during operation is of course crucial for it to be of any real interest, and the possibility of deactivation of the Ag/Al$_2$O$_3$ has to be considered. The catalyst in the study had been used in a previous preliminary test sequence and it had then been stored in air.

To investigate the possible reasons for the low NO$_x$ conversion seen, a core sample of the brick used for engine testing was taken. The weight of the sample was lower than expected and some of the monolith channels were blocked. This means that the monolith brick had a non-uniform coat loading and a lower than expected specific coat loading. The low specific coat loading will affect the deNO$_x$ performance, since Ag/Al$_2$O$_3$ is sensitive to GHSV.

Fig. 8 shows a comparison of standard tests, before and after attempted regeneration. The standard test in the lab-scale reactor showed that the catalyst was almost completely inactive; it only started to show activity at 400 °C. However, a second test following the first one showed that the catalyst had been reactivated. The activity was still low and the catalyst was heated to 500 °C in the reactor in the presence of 1000 ppm H$_2$, 9% O$_2$ and balance N$_2$ to further try to regenerate it. No difference was seen in activity, and the catalyst was heated to 550 °C for 4 h in an oven in an atmosphere of air to burn off soot. After the treatment, the catalyst was completely "clean" and showed no visible traces of soot. The first standard test after the oven treatment showed a small gain in NO$_x$ conversion. A second test showed a somewhat lower NO$_x$ conversion comparable to that before the regeneration attempts of the sample. Prior to the lab-scale and the engine-bench testing,

the catalyst had been stored in air for some weeks. Oxidation of Ag could be one of the deactivation mechanisms seen. Oxidized Ag can be reduced at temperatures below 450 °C, i.e. during the first standard deNO$_x$ test [14,40]. Soot is oxidized by NO$_2$ in the temperature range of 250–400 °C [43], which could explain the increase seen in NO out during engine testing. NO$_2$ from H$_2$ induced NO oxidation being able to oxidize soot might be the reason for the reactivation seen in Fig. 8.

Fig. 9 shows the influence of NO$_2$/NO$_x$ ratio for a 4 wt% Ag/Al$_2$O$_3$ sample. The activity of the sample during a standard test (no NO$_2$) was enhanced after the NO$_2$/NO$_x$ testing campaign compared to before. The higher activity was also seen in later tests and the activation is considered permanent. It is, therefore, concluded that the catalyst needs to be activated before it reaches its maximum activity, similar to what was found in our previous study [20]. In that study, we investigated the sulfur tolerance of Ag/Al$_2$O$_3$ catalysts and related an increased activity for high Ag loading samples to activation by sulfur. The results of this study show that testing under standard deNO$_x$ conditions is, in itself, enough to activate the catalyst. It is speculated that this need for de-greening is related to dispersion and possibly the state of Ag on the catalyst. Further investigations with a similar protocol as in [20] are needed to fully understand the de-greening effect. The presence of NO$_2$ increased the activity below 250 °C and above 300 °C when H$_2$ was co-fed, the effect was largest at the lowest and highest temperatures tested. The first test conducted was the one with an NO$_2$/NO$_x$ ratio of 0.5 which showed a lower activity than the other tests. This lower activity is believed to be related to the sample not being fully activated, it might be that the activation is related to or enhanced by the presence of NO$_2$. We have previously speculated that NO to NO$_2$ oxidation is an important step in the reaction mechanism of NO reduction [17]. The results in this study seem to support that conclusion. The deNO$_x$ activity was very low, when no H$_2$ was co-fed, and it was not dependent of the NO$_2$ level, except at 150 °C, where the NO$_2$/NO$_x$ ratio of 0.95 showed a much higher conversion, and 0.75 showed a somewhat higher NO$_x$ conversion (Fig. 9b). Since the difference in activity was larger between no NO$_2$ at all and 0.25 or 0.95 NO$_2$/NO$_x$ it is concluded that smaller quantities of NO$_2$ is enough to enhance the activity. It is not unreasonable to have 25% NO$_2$ in the exhaust; either from the engine as in this study or after a DOC [1].

Based on the results in Fig. 9 a complete lack of H$_2$ over the catalyst does not seem to be the cause for the low NO$_x$ conversion seen for Ag-only in the engine testing (Figs. 4 and 7). If no H$_2$ was present the NO$_x$ conversion below 250 °C should have been lower and it should have been higher at higher temperatures given the NO$_2$/NO$_x$ ratios in the engine tests. It is concluded that the lower than expected deNO$_x$ activity seen for Ag/Al$_2$O$_3$, both in Ag-only and the combined systems, comes from catalyst deactivation related to soot and possibly Ag oxidation, the lower H$_2$ than was intended and low specific catalyst coat loading giving a high GHSV. The presence of NO$_2$ in the engine exhaust is believed to explain the relatively high NO$_x$ conversion seen when no H$_2$ was fed.

3.2. Transient tests

Fig. 10 shows the NO$_x$ distribution over different temperature intervals for the NEDC. The conditions were, as seen, very demanding for SCR with more than 50% of the total NO$_x$ emitted being emitted at below 150 °C and only 32% above 200 °C. Table 2 shows the gas composition during the NEDC. A further implication of the low temperature was NH$_3$ and H$_2$ dosing. In the standard case, NH$_3$ and H$_2$ were dosed when the temperature was above 150 °C. The temperature was stable above 150 °C after around 830 s. In another case, dosing started when the temperature was above 120 °C (after
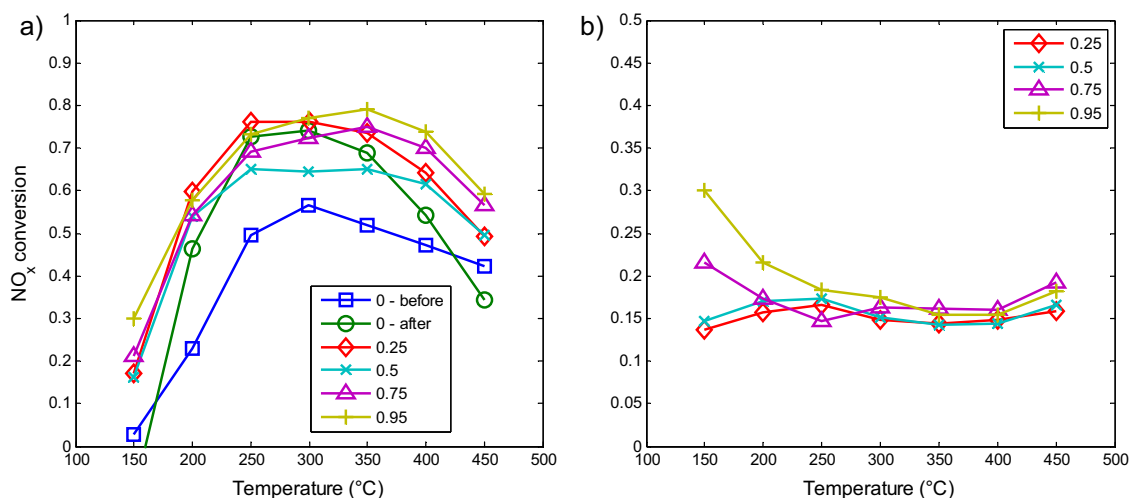
Fig. 9. NO_x conversion as function of temperature for different NO_2/NO_x ratios (indicated in legend); (a) with H_2 and (b) without H_2. Reaction conditions: 500 ppm NO, 500 ppm NH_3, 0 or 1000 ppm H_2, 8% O_2, 12% H_2O and balance N_2, GHSV $\sim$ 30,000 h^{-1}.

Table 2
Typical gas composition during transient engine testing (NEDC).

Component	Concentration (%)	Component	Concentration (ppm)
O_2	10–20	CO	300–1200
H_2O	2–8	HC	150–400[a]
CO_2	0–9	NO_2/NO_x	0.3–0.6[b]

[a] Level was down to 50 ppm in shorter periods of time.
[b] Lower at end of cycle (<0.3).

250 s) to investigate the potential benefit of earlier NH_3 and H_2 dosing.

Fig. 11 shows the accumulated NO_x at the outlet of the tested catalyst layouts. The inlet NO_x amount (measured with the reference MEXA) varied somewhat compared to the reference test. With the difference in the inlet NO_x taken into account, the total NO_x conversion over the cycles was 22, 15, 18 and 22% for Ag-only, Fe-only, dual-brick-Fe and dual-brick-Ag, respectively. This was a small change compared to what is reported in Fig. 11. However, the difference can be assumed to be within the margin of experimental error. There was a large increase in emitted NO_x after around 1100 s of the cycle corresponding to highway driving and the highest engine load (Fig. 2). Since this large increase in emitted NO_x corresponds to the highest temperatures, a large NO_x conversion can be expected. However, the high load resulted in a large increase in GHSV, from maximum 30,000 h^{-1} during urban driving to 70,000 h^{-1} during

the highway part. Ag/Al_2O_3 is sensitive to GHSV [27,29,44], and a GHSV of 70,000 h^{-1} is high. Another issue was NH_3 and H_2 dosing. Due to inconsistent measurements from the NO_x sensors, the level dosed varied. The amount of NH_3 dosed varied between 0.3 and 2 times the NO_x concentration between the start of dosing (after around 830 s) and 1100 s and down to 0.2 of NO_x at the highest flows and temperatures (the set-point was 0.8). H_2 dosing was estimated (no H_2 analysis was available) to be between 0.8 and 2 times the NO_x concentration between the start of dosing and 1100 s and down to 0.2 of NO_x at the highest flows and temperatures (the set-point was 2). Thus, there was a clear shortage of NH_3 and H_2 available for the SCR reaction, when the temperature and emitted NO_x was at their highest, severely affecting the SCR activity. Fig. 12 shows this as the drop in the total NO_x conversion after 1100 s.

By looking more closely at the accumulated NO_x profiles (Fig. 11) and instantaneous total NO_x conversion (Fig. 12) they can roughly be divided into three different parts: The first part was 0–250 s of the NEDC, which is almost one and a half urban cycles. In this part the performance was dual-brick-Ag/Fe ≈ dual-brick-Fe/Ag > Ag-only » Fe-only. The second part was 250–1000 s, urban driving and first part of high-way driving, the temperature was <180 °C; performance was dual-brick-Ag/Fe > dual-brick-Fe/Ag > Ag-only > Fe-only. The last part was >1000 s;
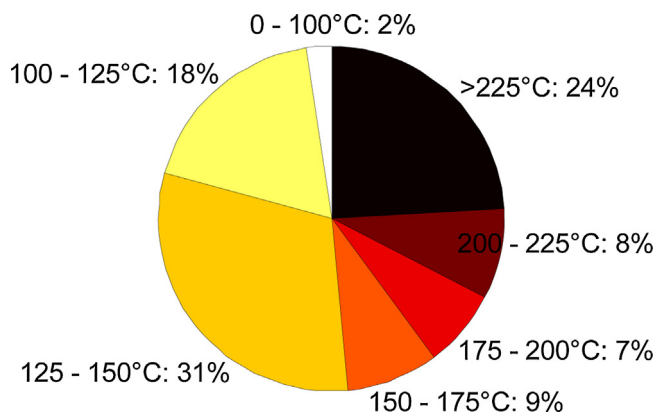

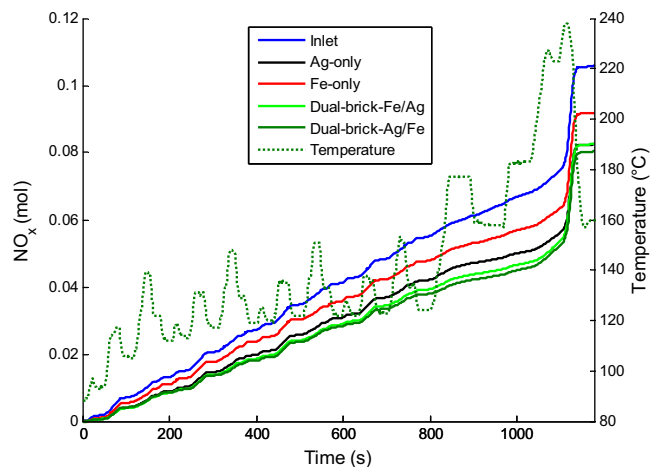**Fig. 10.** NO_x temperature distribution on mole basis measured directly before the catalysts for transient NEDC.

Fig. 11. Accumulated NO_x during NEDC for Ag-only, Fe-only, dual-brick-Fe/Ag and dual-brick-Ag/Fe compared to inlet NO_x, NH_3 and H_2 dosing (only NH_3 for Fe-only).
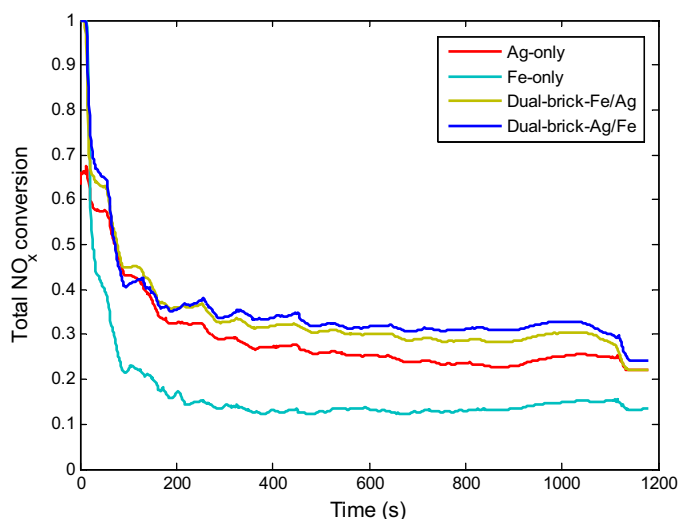
Fig. 12. Total NO$_x$ conversions as function of time during NEDC for Ag-only, Fe-only, dual-brick-Fe/Ag and dual-brick-Ag/Fe, NH$_3$ and H$_2$ dosing (only NH$_3$ for Fe-only).

in this part dual-brick-Ag/Fe did no longer perform better than the other layouts; the order was instead Ag-only > Fe-only ≈ dual-brick-Ag/Fe ≈ dual-brick-Fe/Ag. The difference mainly occurred when the temperature was at its highest (220–240 °C). Given the fact that no NH$_3$ or H$_2$ was dosed until the temperature reached 150 °C (after 830 s) and the low temperatures during the NEDC, it seems unlikely that SCR was responsible for the relatively high NO$_x$ conversion seen in the early stages of the cycle. A 37% total NO$_x$ conversion was, e.g. seen for dual-brick-Ag/Fe after 250 s with a temperature that only reached maximum 140 °C. Even though NH$_3$ was present on the catalyst surface at the start of the NEDC from previous testing, it seems unlikely that any H$_2$ would be present. The fact that NH$_3$ was present at the start of the cycle could be seen as a slow but steady release of NH$_3$, as the temperature was gradually increased (not shown). NH$_3$-TPD confirmed that NH$_3$ would still be present at both Fe-BEA (not shown) and Ag/Al$_2$O$_3$ (Fig. 13a) given the temperatures seen by the catalysts prior to the NEDC (160–270 °C). With the high NO$_2$/NO$_x$ ratios shown (Table 2) and the presence of NH$_3$ over the catalysts, SCR over Fe-BEA is a possibility. The low activity of Fe-only contradicts this theory. Another

possible explanation to the NO$_x$ conversion seen at low temperatures is NO$_x$ storage over the catalysts.

Even though Fe-BEA has been reported to store small amounts of NO$_x$ [5,45], the H$_2$O present in the exhaust is believed to inhibit the storage making this insignificant [5]. Ag/Al$_2$O$_3$ has also been reported to be able to store NO$_x$ [46–50], it has even been considered as NO$_x$ storage catalyst due to its supposedly good storage capabilities [51]. It is vital that O$_2$ is present during adsorption to allow oxidation of NO to ad-NO$_x$ species. NO-TPD was performed for Ag/Al$_2$O$_3$ to investigate the potential of NO$_x$ storage (adsorption at 40 °C). Fig. 13(b) shows two clear peaks, one at approx. 110 °C and one at approx. 410 °C. All catalysts had been used in NO$_x$ containing streams at relatively low temperature (160–270 °C) with only moderate NO$_x$ conversion and relatively high NO$_x$ in the outlet. Peak 2 is therefore assumed to be, at least partly, filled at start of the cycle. The NO$_x$ adsorption capacity from the TPD-results was enough to explain the results seen during NEDC. However, the TPD was performed under dry conditions and H$_2$O will lower the NO$_x$ storage capacity. Brosius et al. [46] showed a noticeable adsorption capacity when NO was replaced by NO$_2$ even when H$_2$O was present. With the results presented in literature [46,51], NO$_x$ storage over Ag/Al$_2$O$_3$ is believed to be a valid explanation of the NO$_x$ conversion seen at temperatures below 140–160 °C during the NEDC in this study.

Fig. 14 shows the inlet and outlet NO$_x$ levels for the tested systems. The NO$_x$ level was in all cases higher or equal at the catalyst inlet compared to the outlet, i.e. no excessive desorption of NO$_x$ during the cycle. The difference between Ag/Al$_2$O$_3$ and Fe-BEA was emphasized. It is clearly seen that Ag-only and the combined layouts showed NO$_x$ conversion right from the start of the NEDC, whereas Fe-only showed NO$_x$ outlet levels closer to the inlet levels. Again this indicates NO$_x$ storage over Ag/Al$_2$O$_3$ as the main mechanism behind the NO$_x$ conversion seen. The temperature never reached higher than 250 °C during the cycle, meaning that part of the NO$_x$ stored on the catalysts likely remained even after the cycle. However, the main part of the NO$_x$ stored will be desorbed during the ramp up in temperature starting after around 950 s. When the temperature increases, so does the activity of the catalysts; this should be seen as a lower NO$_x$ level after the catalysts. However, the NO$_x$ level after the catalyst was similar to the level before the catalysts from 1000 s of the cycle. We believe that two facts are responsible: (1) the GHSV increases with the temperature which will lower the activity of the Ag/Al$_2$O$_3$; and (2) the NO$_x$ desorbed from the catalysts gives a higher NO$_x$ level over the catalyst than
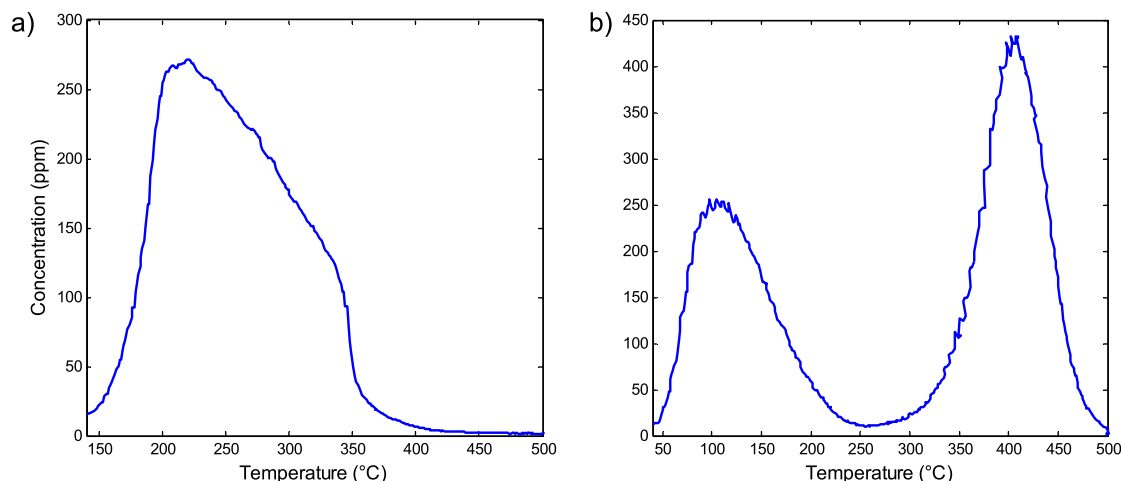

Fig. 13. (a) NH$_3$-TPD, saturation temperature 150 °C, and (b) NO-TPD, saturation temperature 40 °C, of Ag/Al$_2$O$_3$.
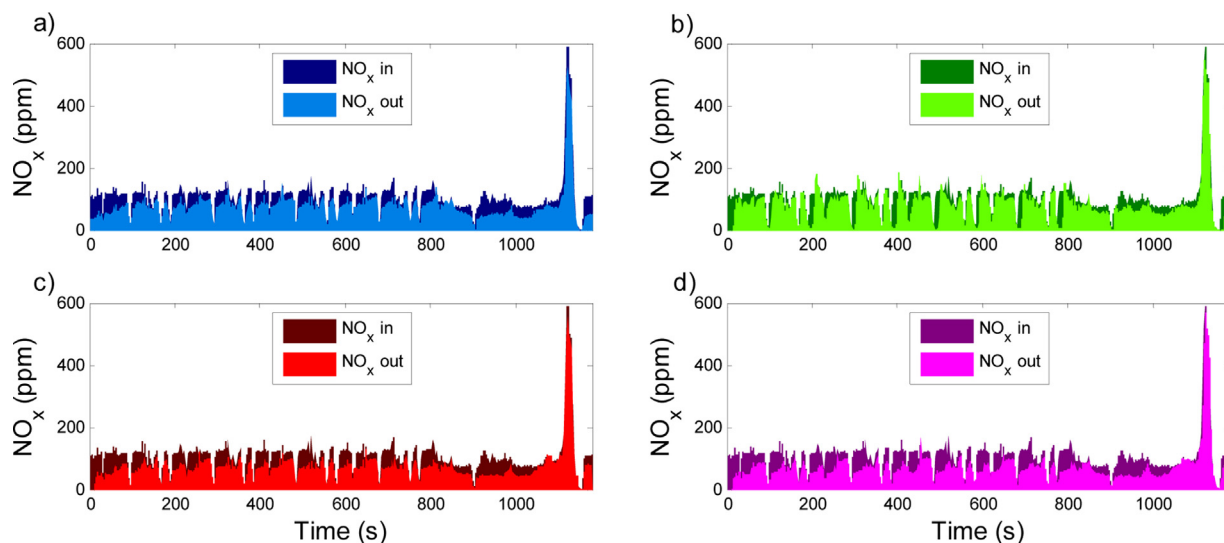
Fig. 14. NO_x before (NO_x in) and after (NO_x out) catalysts during NEDC: (a) Ag-only, (b) Fe-only, (c) dual-Fe/Ag and (d) dual-Ag/Fe, NH_3 and H_2 dosing (only NH_3 for Fe-only).

that of the feed; this excessive NO_x reacts over the catalysts meaning that the NO_x level over the catalyst was higher than expected but still not higher than the inlet level. In other words, the increase in NO_x from desorption was compensated for by the SCR reaction. A NO_x-level that is higher than the feed will also lead to shortage of NH_3 and H_2, since these are dosed based on inlet NO_x-level, further limiting possible NO_x conversion. Catalyst models and advanced dosing algorithms can compensate for this but is beyond the scope of this study.

While NO_x storage is believed to be the main cause of NO_x conversion during the first two identified parts of the NEDC (0–250 and 250–1000 s), SCR of NO_x seems to be the best explanation for the NO_x conversion seen in the last phase, since the rapid temperature rise would desorb NO_x rather than adsorb and store it as believed at the earlier phases. This implies that Ag/Al_2O_3 not only stores NO_x better than Fe-BEA, it also shows a higher SCR activity under NEDC conditions. However, the results indicate synergistic effect of combining Ag/Al_2O_3 and Fe-BEA during parts of the cycle. HC was stored on Ag/Al_2O_3 during the low temperature parts of the cycle and then released, as the temperature increased during the latter part of the NEDC. The total HC conversion over the cycle was 27, 73, 14 and 29% for Ag-only, Fe-only, dual-brick-Fe/Ag and dual-brick-Ag/Fe, respectively. HC-SCR might therefore contribute to the NO_x conversion seen. HC-SCR could be one reason for the advantage of having Ag/Al_2O_3 upstream of Fe-BEA. Another could be that excessive NH_3 adsorption on Fe-BEA hinders the activity over the downstream Ag/Al_2O_3 due to a NH_3 deficit. A step response test in the laboratory set-up (0–300 ppm NH_3) showed that the NH_3 adsorption capacity of Fe-BEA was large enough to give a large delay in NH_3 exiting the catalyst which could potentially affect the performance of the Ag/Al_2O_3, when the latter was placed downstream of the former.

Dosing of NH_3 and H_2 already from 120 °C (after 250 s) compared to dosing from 150 °C (after 830 s) did not give any difference in the total NO_x conversion for the combined layouts. Again, indicating that it was not the SCR reaction that was responsible for the NO_x conversion during the main part of the NEDC. However, a detailed investigation of total NO_x conversion as a function of time (Fig. 15) showed interesting results. The decline in NO_x conversion was more rapid up to approximately 400 s of the cycle, when dosing started at 120 °C as compared to at 150 °C; also seen as a steeper increase in the accumulated NO_x curves (not shown). After approximately 400 s, the NO_x conversion increased, and in
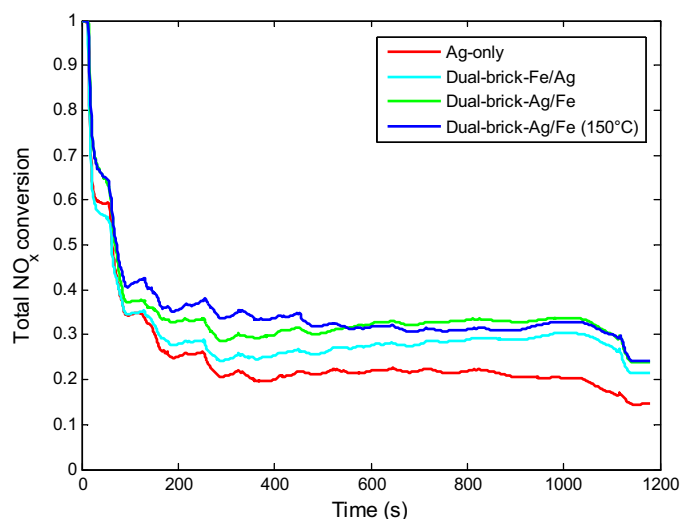

Fig. 15. Total NO_x conversions as function of time during NEDC for Ag-only, dual-brick-Fe/Ag, dual-brick-Ag/Fe with NH_3 and H_2 dosing from 120 °C. Dual-brick-Ag/Fe with NH_3 and H_2 dosing from 150 °C is included for comparison.

the end it reached the same value as in the 150 °C dosing case. This is explained as follows: up to 400 s, NH_3 inhibits NO_x storage and possibly fast-SCR [39]. When the catalyst has been warmed up, there is some SCR activity in addition to NO_x storage, seen as the increase in NO_x conversion. When dosing also starts in the original dosing case, both strategies show the same NO_x conversion. We believe that by optimizing the dosing further, the negative effect of NH_3 can be removed, and a higher total NO_x conversion could be reached. It can thus be concluded that there is some SCR activity even at temperatures down to 120 °C.

4. Conclusions

Stationary engine tests showed clear synergies from combining Ag/Al_2O_3 and Fe-BEA compared to only Ag/Al_2O_3 or Fe-BEA at low temperatures (<270 °C). The unexpectedly low activity of Ag/Al_2O_3 was attributed to deactivation by soot and/or Ag oxidation, low H_2 levels and low specific catalyst loading. Laboratory scale tests of fresh Ag/Al_2O_3 catalyst showed that it was activated by subsequent test runs pointing to the need to de-green the catalyst prior to using

it. The mechanism and a more precise de-greening protocol need to be investigated further. The catalytic activity below 250 and above 300 °C was enhanced by addition of NO_2 as part of the NO_x. An NO_2 level of 25% was enough to give the enhancement; increasing NO_2 only showed a small effect.

Transient NEDC tests showed the same synergistic effects of combining Ag/Al_2O_3 and Fe-BEA seen in the stationary tests. However, the overall cycle NO_x conversion was low which was attributed to low activity of the Ag/Al_2O_3, as seen in the stationary tests. The Ag/Al_2O_3 containing layouts showed a noticeable NO_x conversion from the start of the cycle, i.e. before any NH_2 or H_2 was dosed. We believe that the NO_x conversion seen comes from NO_x storage on the Ag/Al_2O_3.

The Ag/Al_2O_3–Fe-BEA system shows potential, but further studies are needed. Tests with a higher catalyst volume and DPF filter should be conducted to obtain a lower GHSV and avoid poisoning by soot. An advanced dosing algorithm should also be developed that includes NO_x adsorption and desorption for a more accurate NH_3 and H_2 dosing.

Acknowledgements

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